

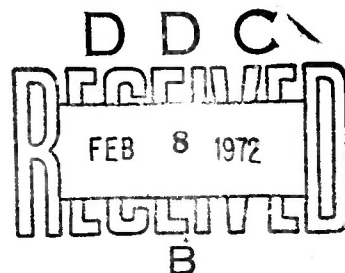
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SOLID PROPELLANT KINETICS

II. THEORETICAL ANALYSIS OF THE
HETEROGENEOUS OPPOSED FLOW DIFFUSION FLAME* +

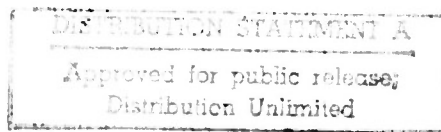
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ABSTRACT

A theoretical analysis is presented of the heterogeneous opposed flow diffusion flame (HOFD). In such a system a gaseous reactant (G) impinges on a solid reactant (S) undergoing sublimation (or vaporization) and a diffusion flame is established at the stagnation point. With increasing mass flux of the gaseous reactant (m_G) the mass flux of solid reactant (m_S) grows until the total consumption rate of reactants reaches a limiting value due to limitations imposed by the kinetics of reaction. The analysis of the axi-symmetrical stagnation point flow with chemical reaction allows evaluation of the kinetics of chemical reaction at temperatures of interest to combustion processes. The theoretical development is applied to the solid-propellant deflagration of an ammonium perchlorate-catalyst-fuel system and the pyrolysis of solid polymers in an oxidizing atmosphere.

Introduction

For the study of reaction kinetics of gas mixtures at temperatures of interest to combustion, the opposed flow diffusion flame (OFD) has been particularly valuable. In experiments employing OFD, one measures the highest mass flux rates of opposing gas jets of fuel and oxidizer that can be consumed in a diffusion flame located in the stagnation region.¹ A series of analytical studies²⁻⁶ examined the relationship between the condition of diffusion flame extinction, the maximum kinetics of gas-phase reaction, and the flame propagation velocity of premixed gases. These theoretical developments were concerned with homogeneous OFD in which the two reactants were introduced at the same mass flow rate per unit area into the reaction region. To apply this technique to solid-propellant combustion kinetics we have treated a theoretical model, the heterogeneous opposed flow diffusion flame (HOFD), in which a gaseous fuel jet impinges on a solid oxidizer surface, such as ammonium perchlorate (AP), which undergoes sublimation. This model considers exothermic chemical reaction in the diffusion flame and heat losses to the environment.

The fundamental difference from the homogeneous OFD is the condition at the solid/gas interface, the source of the oxidizer species in the case of a solid propellant based on AP. Its steady-state surface properties are no longer an independent variable; rather the mass flux of reactant leaving the solid surface is a function of the heat and mass transport, and the thermodynamic properties of the solid. Although similar in some respects to the opposed-flow model chosen by Spalding², our analysis of the HOFD postulates a much more realistic velocity field which satisfies the conditions at upstream infinity.

Mathematical Formulation

As shown schematically in Figure 1, the analysis concerns the opposed jet system and involves a stream of fluid (the gaseous fuel, subscript G) moving in the negative z direction toward a perpendicular flat surface comprising the solid reactive oxidizer (subscript S) undergoing sublimation. The axi-symmetrical stagnation-point flow leads to the following equation for conservation of energy (with the velocity components defined in Figure 1):

$$C_G [(\rho u T)_r + \rho u T/r + (\rho v T)_z] = \lambda (T_{rr} + T_r/r + T_{zz}) + QR_P \quad (1)$$

where C_G is the specific heat of the gas at constant pressure, ρ its density, λ its thermal conductivity, Q the exothermic heat of reaction, and R_P the chemical rate of product generation. Throughout the analysis, the Lewis number is set equal to unity. ($\lambda/C_G \rho D = 1$), and the variable subscripts r and z indicate partial differentiation.

The equation for conservation of total mass is

$$(\rho u)_r + \rho u/r + (\rho v)_z = 0, \quad (2)$$

while that for the mass of species K reads

$$\begin{aligned} &(\rho u Y_K - \rho D Y_{Kr})_r + (\rho u Y_K - \rho D Y_{Kr})/r \\ &+ (\rho v Y_K - \rho D Y_{Kz})_z = R_K \end{aligned} \quad (3)$$

where Y_K is the mass fraction of species K and R_K is its rate of formation in the reaction. The species are taken to be oxidizer X, fuel F, product P, and inert gas I. By introducing the constants $w_K = R_K/QR_P$ we can simplify the equation to

$$\begin{aligned} &\rho u (Y_K - w_K T)_r + \rho v (Y_K - w_K T)_z \\ &= \rho D [(Y_K - w_K T)_{rr} + (Y_K - w_K T)_r/r + (Y_K - w_K T)_{zz}]. \end{aligned} \quad (4)$$

At point G (Fig. 1), the gaseous fuel inlet at upstream infinity ($z = +\infty$) and the dependent variables have the values:

$$T = T_G, \rho u = 0, \rho v = -m_G, Y_K = Y_{KG}$$

At point S on the surface of the solid,

$$\rho u = 0, \rho v = -m_S, -\rho D Y_{KX} = m_S (\delta_{KX} - Y_K),$$

$$\lambda T_z = m_S [L + C_S (T - T_A)]$$

where L is the latent heat of vaporization, C_S the heat capacity of the solid, T_A is the ambient temperature at infinity in the solid, and $\delta_{KX} = 1$ if $K = X$ and is zero otherwise.

At this point the simplifying assumptions are made that (1) specific heat, density, and transport coefficients may be replaced by constant average values, and (2) radial diffusion may be neglected with respect to convection and axial diffusion. Thereby the equations for conservation of energy and mass of species K reduce to

$$C_G (\rho u T_r + \rho v T_z) = \lambda T_{zz} + Q R_P \quad (5)$$

$$\rho u (Y_K - w_K T)_r + \rho v (Y_K - w_K T)_z = \rho D (Y_K - w_K T)_{zz} \quad (6)$$

Along the axis of symmetry $u = 0$, so that the equations contain only functions of z and derivatives with respect to z . Let $y(z)$ be the solution on $r = 0$ of the equation

$$\rho v y' = \rho D y'' \quad (7)$$

Then

$$Y_K - w_K T = A_K + B_K y \quad (8)$$

where A_K and B_K are constants of integration, and the energy equation reads

$$\lambda T_{yy} (y')^2 + Q R_P = 0 \quad (9)$$

Solution of the Equations

It is now assumed that $(y')^2$ has a reasonable form as a function of z so that the distribution of reaction rate can take that form:

$$R_P = (\lambda J/Q) (y')^2 \quad (10)$$

where J is a constant. Then

$$T = A + By - Jy^2/2 \quad (11)$$

where A and B are constants. Thus all dependent variables have explicit forms as functions of y on $r = 0$.

A reasonable form for y is

$$y = \tanh az \quad (12)$$

with some constant a . One finds on $r = 0$ by Eq. (7)

$$\rho v = -2a\rho D \tanh az \quad (13)$$

so that to fit the condition at G

$$a = m_G/2\rho D \quad (14)$$

An extension of ρv to points off the axis of symmetry which gives a jet-like flow is

$$\rho v = -m_G \tanh az \operatorname{sech}^2(br^2/2) \quad (15)$$

where constant b can be related to the jet width.

The equation for conservation of total mass can then be solved to give

$$\rho u = (a m_G/br) \operatorname{sech}^2 az \tanh (br^2/2) \quad (16)$$

This solution satisfies the boundary condition at G, $\rho u = 0$ at $z = \infty$, but at the solid surface ($z = z_s$), $\rho u = 0$ only on $r = 0$. Since the solution is needed on $r = 0$, this error is not likely to affect the results seriously.

The solution for T on $r = 0$ satisfying the condition at G is

$$T = T_G + B^*(1-y) - J(1-y)^2/2 \quad (17)$$

where B^* is a convenient form for the remaining constant of integration. The conditions at the solid surface determine $y = -m$ and

$$B^* = \frac{\{(1+m)^2 J [m C_S + (1-m) C_G] - 2m [L + C_S (T_G - T_A)]\}}{(1+m) [2m C_S + (1-m) C_G]} \quad (18)$$

where $m = m_S/m_G$. This ratio is restricted to $0 < m < 1$ by Eq. (15).

Boundary conditions at S and G similarly determine the constants of integration A_K and B_K in the solution forms for the Y_K .

The maximum temperature is

$$T_M = T_G + B^{*2}/2J \quad (19)$$

and it occurs at $y = y_M$, where $y_M = 1 - B^*/J$. It can be readily determined from the reaction rate R_{PM} at point M:

$$J = 4\lambda Q R_{PM}/m_G^2 (1 - y_M^2)^2 \quad (20)$$

Application to Heterogeneous Combustion System

For the special case for which (1) the reaction rate is of first order in the fuel and oxidizer concentrations, (2) the conductive heat loss into the solid phase $[C_S (T_S - T_A)]$ is negligible relative to the heat of sublimation L, and (3) the temperature maximum is located at the stagnation point ($y_M = 0$), the equations just derived become greatly

simplified. For such a case the rate of product generation is given by

$$R_p = \rho^2 (Y_F) (Y_X) Z \exp (-E/RT) \quad (21)$$

where Y_F and Y_X are the weight fractions of fuel and oxidizer, E the activation energy, R the gas constant, and Z the preexponential term in the Arrhenius expression. This equation applies equally at the stagnation point where $R_p \rightarrow R_{PM}$ and $T \rightarrow T_M$. To simplify the calculation, we make the additional approximation that at this point Y_F and Y_X are unity. Under these conditions Eq. (20) reduces to

$$\dot{m} = 4\rho^2 \lambda Q Z \exp (-E/RT_M) / m_G^2 \quad (22)$$

Finally, in combination with Eqs. (18) and (19), after neglecting mC_S with respect to $(1-m)C_G$, one obtains

$$m_G^2 = 2\rho^2 \lambda Q (C_G/L) (1-m^2) Z \exp (-E/RT_M) \quad (23)$$

$$\text{where } T_M = T_G + [L/C_G (1-m^2)]$$

The function given by Eq. (23) has the properties depicted in Figure 2. With increasing mass flux of the fuel component (m_G), the steady-state mass flux of solid oxidizer (m_S) grows until it attains a maximum value at the limiting ratio $m^* = m_S^*/m_G^*$. Further increase in m_G causes the kinetics of reaction to limit further consumption of reactants and leads to extinction. At the maximum point $d m_S / d m_G = 0$ or $d m_G / d m = -m_G / m$ so that

$$E' = \left[\frac{2m^{*2} - 1}{m^{*2}(1-m^{*2})} \frac{(1+L'-m^{*2})^2}{L'} \right] \quad (24)$$

where $E' \equiv E/RT_G$ and $L' \equiv L/C_G T_G$.

In Table 1 we have computed E' for different values of m and L' .

Also for values of m^{*2} near unity Eq. (24) reduces to

$$E' \cong L'/(1-m^{*2}) \quad (25)$$

It is apparent that the activation energy for the fuel-oxidant gas-phase reaction may be evaluated from the critical mass flux ratio m^* . An interesting application of this theoretical model is to be found in the pyrolysis measurements of polymethyl methacrylate (PMM) by McAlevy and coworkers.⁷ In an experimental study involving a stream of oxygen impinging on the solid polymer, the linear regression rate of the polymer attained a maximum corresponding to a critical mass flux ratio of $m^* = m_S^*/m_G^* = 1.5 \times 10^{-2}$. Based on an effective endothermic heat of sublimation⁷ of about 1000 cal/g one calculates by substitution into Eq. (25) an activation energy of 8 kcal/mole for the gas-phase combustion process of PMM-oxygen. As shown in a subsequent publication⁸ we have used the HOFD theory in an evaluation of the reaction kinetics of the system ammonium perchlorate-catalyst-hydrocarbon. Further theoretical work is in progress to remove the restriction of $m^* < 1$ from the analysis, so that the model may have applicability to a wider range of combustion systems.

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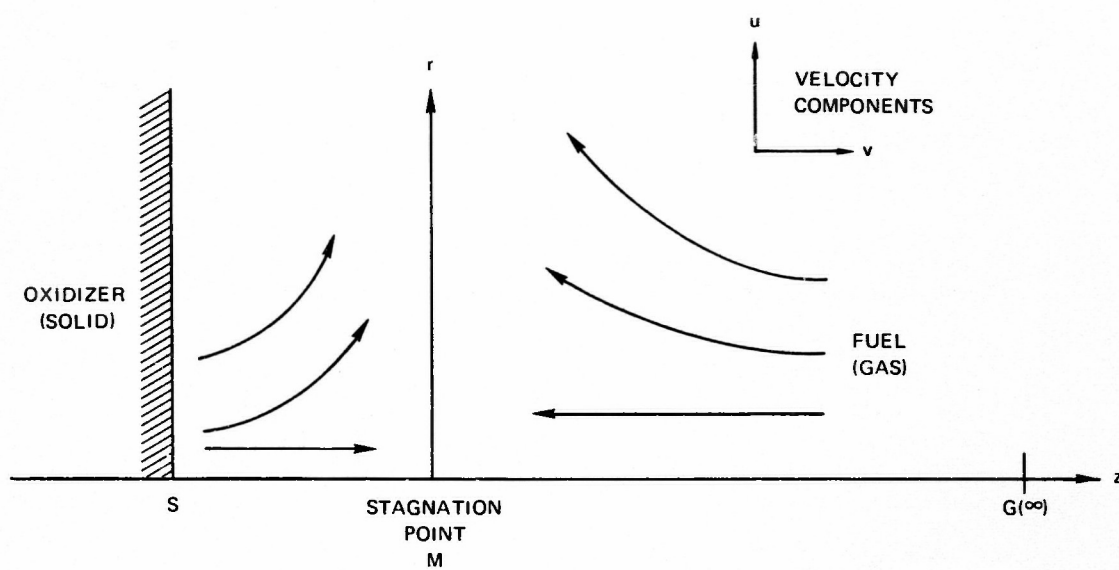
Table 1

COMPUTATION OF E' (Eq. 24)

$(m^*)^2$ L	E'				
	0.1	0.3	1	3	10
0.6	2.08	1.35	1.63	3.23	9.0
0.8	3.38	3.11	5.40	12.8	39.0
0.9	3.55	4.71	10.7	29.3	90.5
0.95	4.26	7.70	20.8	58.8	193.0

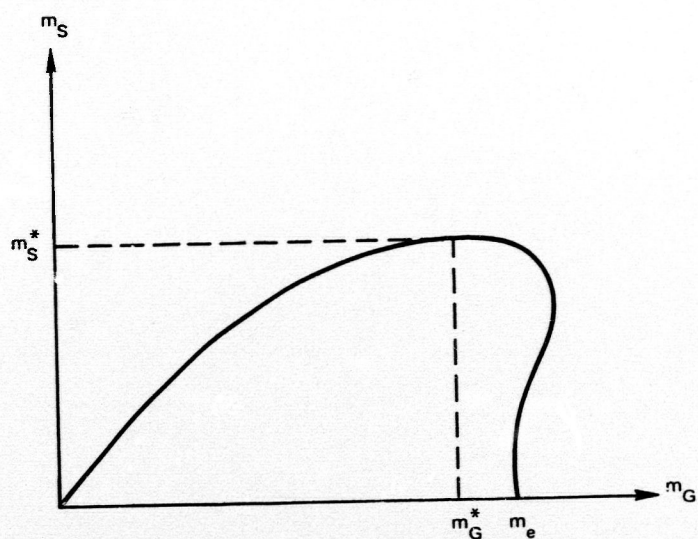
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1. Flow Field in Heterogeneous Opposed Flow Diffusion Flame
2. Theoretical Relation between Mass Flux of Solid (m_s) and Gas (m_g) Reactants in the Heterogeneous Opposed Flow Diffusion Flame (m_e = extinction condition).



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FIGURE 1 FLOW FIELD IN HETEROGENEOUS OPPOSED FLOW DIFFUSION FLAME



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FIGURE 2 THEORETICAL RELATION BETWEEN MASS FLUX OF SOLID (m_s) AND GAS (m_g) REACTANTS IN THE HETEROGENEOUS OPPOSED FLOW DIFFUSION FLAME (m_e = extinction condition)